On the Physical Nature of Uranyl Charge Transfer Vibronic Interactions

X. Y. Chen[1], L. F. Rao[2], and G. K. Liu[1*],
[1] Chemistry Division, Argonne National Laboratory, Argonne, IL 60439
[2] Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

ABSTRACT

We address the electronic properties of uranyl ions in solids and solutions with an emphasis in theoretical understanding of charge transfer vibronic transitions and luminescence dynamics the O-U-O species. A general theory of ion-phonon interaction has been modified for modeling and simulating multi-phonon vibronic spectra. Spectroscopic data for uranyl ions in crystals and solutions have been analyzed to achieve a predictive understanding of the uranyl-ligand vibronic interactions. By adjusting the Huang-Rhys ion-phonon interaction parameters, an excellent agreement between theory and experiment has been accomplished for uranyl ions in the ligand environments we studied. Our modeling and simulation provide insights into the physical nature of uranyl vibronic interaction and its influence on spectroscopic properties, which are commonly utilized in characterizing photochemical properties of uranyl in complexes.

INTRODUCTION

From uranium to americium, the lighter elements in the actinide series often bind with two oxygen anions to form actinyl ions. The uranyl ion (UO_2^{2+}) with a bond distance in the range of 175-185 pm is extraordinarily stable in solutions as well as in crystals and glasses. The environmentally sensitive optical spectra of uranyl species, arising from O-U-O charge transfer (CT) transition, have been widely used for characterization of local structure and coordinations around the uranyl.   It is also well known that vibronic states originating from the charge transfer-vibronic interaction are quite localized due to the short bond distance as well as high vibrational energy (750-900 cm^{-1}). As a result, the absorption and emission spectra of the UO_2^{2+} ion in single crystals such as $Cs_2UO_2Cl_4$ indeed exhibit extremely sharp lines [1], in which the progressions are exclusively induced by the totally symmetric local mode. Unlike the vibronic spectra of f-d or f-f origins for lanthanide and actinide, the CT vibronic spectra of UO_2^{2+} apparently do not include the contributions from coupling to the lattice acoustic modes other than to the local stretching mode. As a result, the uranyl vibronic spectra are simpler than that coupled to the f-f and f-d transitions [2-6].

Although, optical spectroscopy and laser-induced fluorescence are widely used in actinide chemistry and speciation, the nature of photochemistry and photophysics of uranyl complexes is currently lacking a fundamental understanding in general. A dimensionless Huang-Rhys parameter (S), which is closely related to the transition mechanism of optical centers in the host, is generally used to represent the extent of electron-phonon coupling [7]. Theoretical work on the basis of Franck-Condon (FC) transition was reported for comparison with experimental results from rare earth ions in crystals [2-6,8]. However, the line shape of multiphonon sidebands in vibronic spectra as a function of temperature and coupling strength is ambiguous, thus not often used in analysis of experimental data. Recently, we realized that the spectra of multiphonon vibronic transitions of heavy element ions in crystals can be analyzed using a single-mode or

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coupled multi-mode approximation of electron-phonon coupling and the contribution from the lattice acoustic modes (the so-called secondary adiabatic approach) may be approximately treated as line broadening [5,6]. In this approach, it is convenient to theoretically fit the experimental spectra so as to extract the information on how the line shape and vibronic patterns are influenced by localized phonon modes, temperature, and radiation damage.

THEORETICAL MODEL

Recently we proposed a model to describe the multiphonon vibronic structure in the case of intermediate or strong electron-phonon coupling. In this model, multi-phonon modes are strongly coupled to the electronic states and their interference is evaluated. At the same time, the observed broad bands are attributed to the contributions from acoustical phonon modes and are taken into account by an effective acoustical phonon mode [6]. According to the selection rules for a FC transition, the allowed vibronic modes that are observed in the progression of a multi-phonon vibronic spectrum have generally the characteristics of totally symmetric stretching modes (or breathing modes). This model is also applicable to the CT vibronic spectra of UO_2^{2+}. Specifically, for UO_2^{2+}, only one mode, namely the O-U-O stretching mode, is taken into account. The over-all spectral function of intensity, determined primarily by the high frequency local mode with an angular frequency of Ω and a Huang-Rhys parameter of S_Ω, can be expressed as [5,6]

$$I(E) = C|M|^2 \exp[-(2n+1)S_\Omega] \sum_N \left(\frac{n+1}{n}\right)^{N/2} I_N\left(2S_\Omega\sqrt{n(n+1)}\right) \cdot g(E) \cdot \left(\frac{E_{ZP} \pm N\hbar\Omega}{E_{ZP}}\right)^{5/2 \mp 3/2} \quad (1)$$

where

$$n = \frac{1}{\exp(\hbar\Omega/kT) - 1} \quad (2)$$

$$g(E) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(E_{ZP} \pm N\hbar\Omega - E)^2}{2\sigma^2}\right] \quad (3)$$

C is a constant; E_{ZP} is the zero-phonon line (ZPL) of the electronic transition; $\sigma = \sigma_{inh} + \alpha T^{1/2}$ is the Gaussian line-width originating from both inhomogeneous broadening and phonon induced homogeneous line-broadening, and α is usually treated as an adjustable parameters. $I_N\left(2S_\Omega\sqrt{n(n+1)}\right)$ is the Nth order modified Bessel function of the first kind; "+" in the parentheses corresponds to the absorption/excitation process, and "–" denotes emission process; $|M|$ is the transition matrix element of the ZPL induced by electric-dipole (ED), magnetic-dipole (MD), or forced electric-dipole; the last term with a power of 4 (or 1) in Eq.(1) refers to the frequency correction factor for emission (or excitation/absorption) intensity [9].

The variation of the axial U-O bond distance between the excited state and ground state involved in the CT transition can be calculated according to [9,10]:

$$\Delta R_{U-O} = \frac{\Delta Q}{\sqrt{2}} = \sqrt{\frac{\hbar S_\Omega}{m\Omega}} \quad (4)$$

where m is the mass of oxygen ligand. For UO_2^{2+}, the axial U-O bond distance in the excited state is a little bit longer than in the ground state. However, it is not always true for d-f vibronic

transitions. Tanner *et al* [11] and Barandiaran *et al* [12] recently showed that, according to their quantum chemical calculation, the Ce-Cl or (Pa-Cl) bond distance in the excited state is shorter than that in the ground state.

RESULTS AND DISCUSSION

UO_2^{2+} in Cs_2ZrCl_6

This crystal is monoclinic, having space group $C_{2/m}$. Each $UO_2Cl_4^{2-}$ unit has exact C_{2h} symmetry, but is slightly distorted from D_{4h} symmetry. The experimental emission spectrum at 20K was reported by Metcalf *et al* [1], by monitoring the charge transfer transition $E_g \rightarrow A_{1g}$ (D_{4h}), with ZPL at 19692 cm^{-1}. The only progression is caused by the O-U-O symmetric stretch (A_{1g}) mode. The ZPL is of MD nature due to centrosymmetric site-symmetry. The other 3 false-origin lines at 19570, 19437, and 18791 cm^{-1} are non-FC allowed transitions, which is of forced ED nature induced by ungerade vibronic modes (B_{1u}, E_u and A_{2u}) respectively, in agreement with the selection rules of vibronic transition. These lines can serve as origins for FC-allowed progressions in the symmetric stretching frequency (v_1 at 819 cm^{-1}). Obviously, due to the ungerade symmetry, progressions of the localized vibronic modes of v_2 (A_{2u}), v_{10} (B_{1u}) and v_3 (E_u) themselves should not be observed. As shown in Figure 1, the calculated line intensities agree well with those experimental lines. It should be pointed out, that the experimental ZPL intensity is much lower than the calculated because of self-absorption in the true electronic origin transition. According to the fit to the experimental emission spectra, the Huang-Rhys parameter (S) for the symmetric stretching mode (v_1 at 819 cm^{-1}) is determined to be 0.90, in consistence with [1]. The intensity ratios of three false ZPLs of Forced ED nature to the true ZPL of MD nature are estimated to be 1.45, 0.41 and 0.16 for the ungerade local modes of v_2 (A_{2u}), v_{10} (B_{1u})
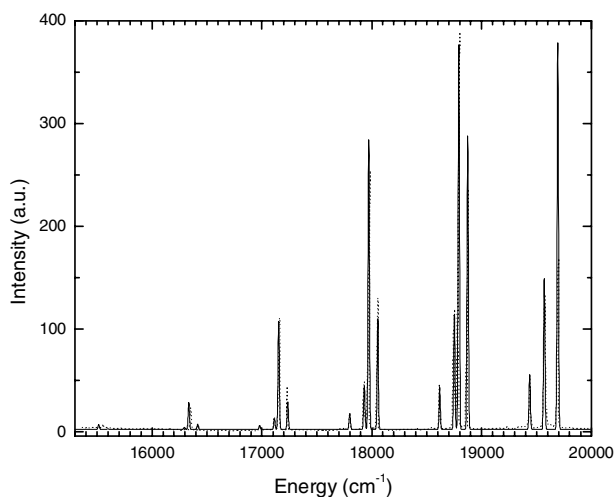
Figure 1 Comparison between calculated (solid) and experimental (dot, from [1], T = 20 K) emission spectra of multiphonon vibronic transitions originating from $E_g \rightarrow A_{1g}$ in $Cs_2ZrCl_6:UO_2^{2+}$ crystal.

and v_3 (E_u) respectively. The linewidth (σ) of each multiphonon line is assumed to be 6.0 cm^{-1} at

20K. S=0.90 (ν_l at 819 cm^{-1}) indicates that U-O bond distance is 4.8 pm longer in the excited state than in the ground state.

UO_2^{2+} in solution

Numerous studies have been conducted on the vibonic spectra and on the structure for the hydrolysis products of uranium(VI) in aqueous solutions [13-18]. As an example, we focus on the optical properties of (3,5) species, namely, $(UO_2)_3(OH)_5^+$, which is prepared according to the following hydrolysis process: $3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+$. The detailed sample preparation via the hydrolysis of uranium(VI) in tetraethylammonium perchlorate has been reported in [19]. The total concentration of uranium in the solution is 0.0001 M. Speciation calculation indicates that $(UO_2)_3(OH)_5^+$ species is dominant in the solution (~ 80%) at 293 K.

The observed fluorescence was induced by a tunable pulsed dye laser in pumping the uranyl charge transfer transition. The pumping laser was tuned between 423-425 nm in the maximum absorption region of uranyl in the solutions. The quartz bottles that contained the sample solutions were inserted into the modules of a temperature controlled thermal bath. The fluorescence decay measurements were performed on the selected emission at 515 nm.

The fluorescence spectra and lifetimes were measured at various temperatures from 20 to 80°C. When the temperature was increased, the fluorescence lifetime decreased, whereas little change was observed in the patterns of the emission spectra, as shown in Figure 2. This implies that the phonons involved in the vibronic transitions have the same frequencies in this temperature region. Unlike UO_2^{2+} in a crystal, the observed vibronic lines in the solution are too broad to distinguish those contributions from ungerade vibrational modes coupled to the true ZPL. Therefore only the true ZPL induced progression is taken into account in our analysis.
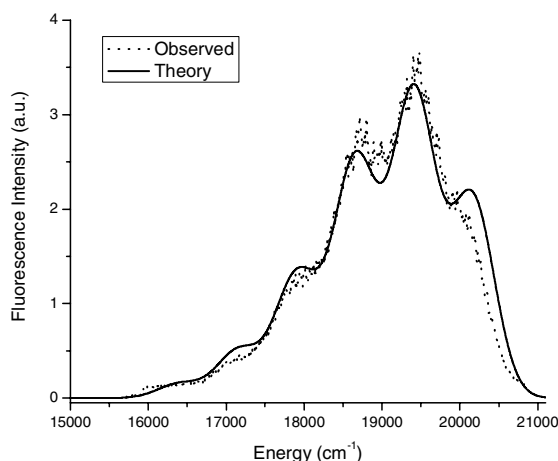
Figure 2 Comparison between calculated (solid) and experimental (dot) emission spectra of multiphonon vibronic transitions between the CT states of $(UO_2)_3(OH)_5^+$ solution at 293K.

According to our model fit as shown in Figure 2, the O-U-O stretch frequency is determined to be approximately 750 cm^{-1}, the Huang-Rhys factor of this totally symmetric mode is 1.80, and the linewidth (σ) of each multiphonon line is about 280 cm^{-1}. The Huang-Rhys factor of 1.80

indicates that axial U-O bond distance is 7.1 pm longer in the excited state than that in the ground state. The uranyl stretch frequency is quite low in comparison with that of uranyl in solids and in aqueous solutions of low pH, which is typically higher than 800 cm^{-1} [20]. The mechanisms that lead to the significant changes of the urayl vibration frequency in the species we studied in the present work are not clearly understood and further investigation is needed.

It is observed that the fluorescence of (3,5) species decays as a single exponential function of time at various temperatures. The lifetime decreases significantly from 25.8 μs at 20°C to 2.4 μs at 80°C. The temperature dependence of the fluorescence lifetime of (3,5) species obeys the Arrehnius law [16,18-19]. Different from UO_2^{2+} in the crystal or glass, the nonradiative decay pathway for lifetime shortening in the aqueous solution is mainly of chemical nature, influenced by pH and temperature of the solution.

CONCLUSIONS

Based on the approximation of single configuration coordinate and Huang-Rhys approach, a general theory of electron-phonon interaction has been modified for modeling and simulating multi-phonon vibronic spectra of uranyl CT transition. The vibronic spectra of UO_2^{2+} in Cs_2ZrCl_6 crystal and $(UO_2)_3(OH)_5^+$ solution obtained from the model fit agree well with those experiments.

The bond distance lengthening of UO_2^{2+} in the excited state of (3,5) species is much larger than those in the solids. It is possible to confirm the reported bond distance variation by utilizing in-situ EXAFS measurement immediately after the laser excitation. It seems that the axial U-O bond is significantly weakened for (3,5) species in the solution. Compared to the free UO_2^{2+} species in the acidic solution [14,15], the ZPL position for the CT origin has shifted significantly toward the red (20160 cm^{-1}), vibronic frequency is significantly lowered from 870 cm^{-1} to 750 cm^{-1}, and the Huang-Rhys parameter is much larger (from a typical value of 1.2 to 1.8). The fluorescence lifetime of UO_2^{2+} in the solution is more complicated and temperature-sensitive due to the efficient electronic mobility in solution and temperature-dependent hydrolysis.

ACKNOWLEDGMENTS

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